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TITLE   CONDUCTING HYBRID POLYMERIC SYSTEMS

AUTHOR(S)   Mahmoud Aldissi, MST-7
J. W. White, The Australian Nat'l University
Stephen Agnew, INC-4
Betty S. Jorgensen, MST-7

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Los Alamos   Los Alamos National Laboratory
Los Alamos, New Mexico 87545

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CONDUCTING HYBRID POLYMERIC SYSTEMS

M. Aldissi, J. W. White@, S. Agnew and B. S. Jorgensen

Los Alamos National Laboratory, Los Alamos, NM 87545, U.S.A.
@   The Australian National University, Canberra A.C.T. 2601,
Australia

INTRODUCTION

In this paper we discuss the synthesis and properties of
block and alternated copolymers as hybrid, multiphase polymers
which are characterised by a high electrical conductivity.
Conventional block copolymer systems possess, in general,
properties that are close to the average "weighted" properties of
their various homopolymer components. The properties of the
corresponding random copolymers could be quite different. On the
other hand, alternating copolymers do not seem to exhibit any
particular properties that are not found in the block or random
copolymers. In our studies, we wanted to take advantage of the
opportunities that could be offered to the polymer scientist by
copolymerisation for gaining insight into important areas related
to electrical conduction such as morphology, phase separation,
polymer-polymer interfaces and solubility. Also, copolymerisation
is technologically important for it allows us to tailor-make
products with specifically desired properties. However, the
utility of copolymerisation involving conjugated, rigid
components could be different from that of conventional polymers.
We will focus in this paper on the synthesis and properties of
various materials:

o   Rod-coil systems such as polyisoprene/polyacetylene diblock
      copolymers: resonance raman and small angle neutron
      scattering studies correlated to conductivity .

o   Alternating copolymers such as poly (arylpyrroles):
      electrochemical synthesis and characterisation.

ROD-COIL COPOLYMER SYSTEMS

The diblock copolymers which are studied here consist of a
rigid, conjugated block (polyene or polyacetylene) and a flexible
block such as polyisoprene. The materials are synthesised via
coordination polymerisation of acetylene by a polymeric catalyst
formed by the reaction of tetrabutoxytitanium with e.g.,
poly(isoprenyllithium), as described earlier (1),. The
conductivity measurements at room temperature of the doped
materials showed that the electrical properties are strongly
dependent upon the copolymer composition, i.e., the relative
amount of polyene segments, and that conduction occurs by
percolation (Fig. 1) with a threshold of approximately 16% volume

fraction of polyacetylene (2). Scanning electron microscopy gave a very good qualitative correlation to such properties and showed that the morphology depends quite strongly upon the composition. In order to understand the conduction process in these systems, we have carried out several studies to characterize chain morphology, aggregation and/or phase separation in the various compositions.

1) Raman Scattering and Chain Morphology

Resonance raman scattering (RRS) of a polyacetylene sample gives information about conjugation lengths and distributions. This technique constitutes a sensitive probe of the quality of a given sample. Polyacetylene spectra are usually characterized by two main features at raman shifts around 1100 wn and 1500 wn for C-C and C=C bonds respectively. Raman shifts, lineshapes and intensities of these features vary with the laser excitation wavelength. Previous RRS studies (3-5) of polyacetylene chains have been marked by the absence of an internal standard, therefore, the excitation profiles and related studies done in the past could not be totally accurate due to the insolubility of the samples. We report here, for the first time, true excitation profiles of soluble polyacetylene/polyisoprene copolymers in which the internal standard used to calibrate the intensities of the various peaks is that of the solvent which in this case is toluene (peak at 1004 wn) (Fig. 3). As for insoluble polyacetylene, a shift in the positions of the various peaks for different excitation wavelengths is observed (Fig. 2). In contrast to what has generally been assumed, the 1294 feature, used in other studies (3,4) as an internal standard is indeed resonance enhanced and its profile follows that of the short conjugated segments. Our measurements allow for the first time quantitative comparison between short and long conjugation length portions of the copolymer and therefore can be applied to polyacetylene and other conjugated polymers that lack the presence of an internal standard. In our samples, we have a 2/3 ratio of C=C bonds between short and long segments. The long segments excitation profile peaks at 2.15 eV and that of the short segments at 2.6 eV. Based on the extrapolation of Kudson et al. (6), there are 31 C=C and 11 C=C in the long and short conjugated segments respectively. Using our data, the short chain length mole fractions in our soluble polyacetylene and insoluble polyacetylene films are 65% and 28% respectively. Our RRS results are interpreted in that the microscopic morphology of the soluble copolymer is similar to that of conventional polyacetylene despite the presence of polyisoprene blocks. Also, we assume that the bimodal distribution which corresponds to long and short segments associated with those portions of the polymer that are bound in one-dimensional crystalline fibrils, while short conjugated segments represent regions in which the chain must kink or fold to accommodate the fibrils. The presence of more of these kinks in the soluble materials due to the accommodation of polyisoprene blocks which can be thought of as protruding from the fibrils, forming a "glue" to bind to other fibrils.

2) Small Angle Neutron Scattering and Aggregation

The materials have been studied as a function of the concentration of polyacetylene in the copolymers for 10%, 20% and 30% polyacetylene volume fractions which are below, at and above the percolation threshold mentioned above. To gain contrast in the scattering, the polyacetylene blocks were fully deuterated. This resulted in very strong scattering. The 30% solid sample showed a scattering with a low Q slope near unity indicating that the $(CD)_x$ scattering species are in near cylindrical form of a radius 26.1 Å. The observed differences at high Q arise because the indicated polyene rods are not monodisperse in diameter. Therefore, the evidence points to uneven rod-like structures of about 1000 Å length and 26.1 Å diameter. A 30 Å diameter is found if a fractal model fitting program (7) is employed. The data indicate that the micellar aggregates in the two other samples are spherical with an increasing size when the volume fraction of polyacetylene increases. Aggregate size and dimensionality in the various cases are summarized in Table 1.

TABLE 1: **Fractal Analysis of polyacetylene-polyisoprene diblock copolymers**

% $(CD)_x$	Radius Å	Aggregate size/Å	Dimensionality
30	30	1500	1.5
20	3	500	2.4
10	2.5	120	2.6

The control of these structures is an exciting possibility under study, but the qualitative result of rod-like micellar texture at 30% and the easy percolation of long rods explains the observed conductivity threshold: the material is thus a conductor in a rubbery (polyisoprene) matrix.

ALTERNATING COPOLYMERS - POLY (ARYLPYRROLES)

Our focus has been on newly synthesised polyheterocycles in which the repeating unit is an arylpyrrole moiety of the general formula shown below, for the following reasons:

Ar = THENYL

FURYL

PHENYL

R_1 and R_2

H or ALKYL GROUPS
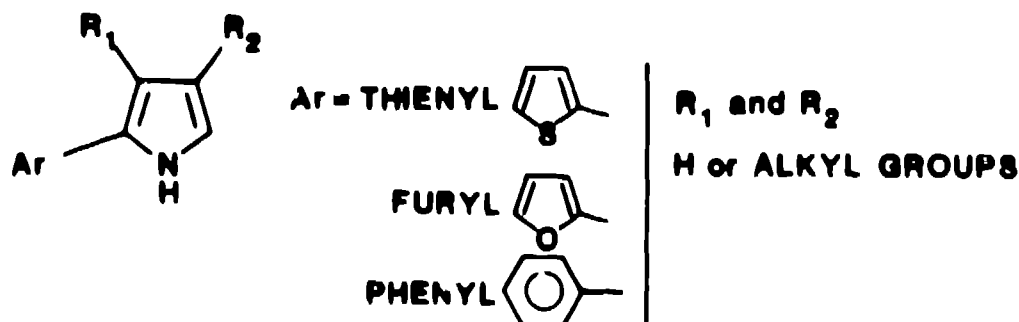
o   The decrease in disorder by reducing the number of coupling sites during the electrosynthesis, and therefore, the decrease of the amorphous character that dominates known polyheterocycles.

o   The π system in arylpyrroles is such that their electron density is higher than in pyrrole. The electron delocalisation causes the polymerisation to occur easily resulting in soluble materials necessary for studying the single chain behavior.

o   Arylpyrroles could lead to conjugated "diatomic" polymers with theoretically well defined excitations.

We have shown for the first time that arylpyrroles can be polymerised electrochemically leading to alternating copolymers (8) and therefore could be the first synthetic conducting A-B polymer which could be used to test the theoretical predictions on the particle excitations: solitons or polarons in the bleached state and polarons and/or bipolarons in the doped (oxidised) state. Their electrochemical synthesis is performed in the same way as for polypyrrole or polythiophene. Due to the electron delocalisation in the monomer units the polymerisation occurs easier than in the latter two compounds. In fact, an applied potential of 0.25 V $\underline{vs}$ Ag/AgNO$_3$ is enough to initiate the polymerisation of thienylpyrrole or furylpyrrole at the surface of an anode. The potentials needed for polymerising thiophene or pyrrole are higher. The cyclic voltammograms of thienylpyrrole exhibit one oxidation peak and a corresponding reduction peak at potentials different from those of thiophene and pyrrole separately. One important feature of poly(arylpyrrole)s is their solubility in the organic medium in which they are prepared, particularly THF, propylene carbonate (PC) or acetonitrile. The color of the solutions varies with the solvent. Preliminary studies indicate that the molecular weights are higher than 20,000. However, low molecular weight fractions and large aggregates are obtained in each case. Polymer films could also be obtained along with the polymer solution, particularly when a poor solvent is used. Conductivities of films in the range 1 - 10 S/cm are generally obtained. The optical absorption spectrum of poly(thienylpyrrole) shows one single peak in the visible at 2.8 eV which is intermediary between polythiophene and polypyrrole (Fig. 4). The optical spectra of the various synthesised materials show peaks that correspond to polaronic and bipolaronic species at energies that depend upon the electrolyte system used and the repeat unit. Optical absorption characteristics are shown in Table 2.

TABLE 2: Optical Absorption Maxima of Poly(arylpyrrole)s

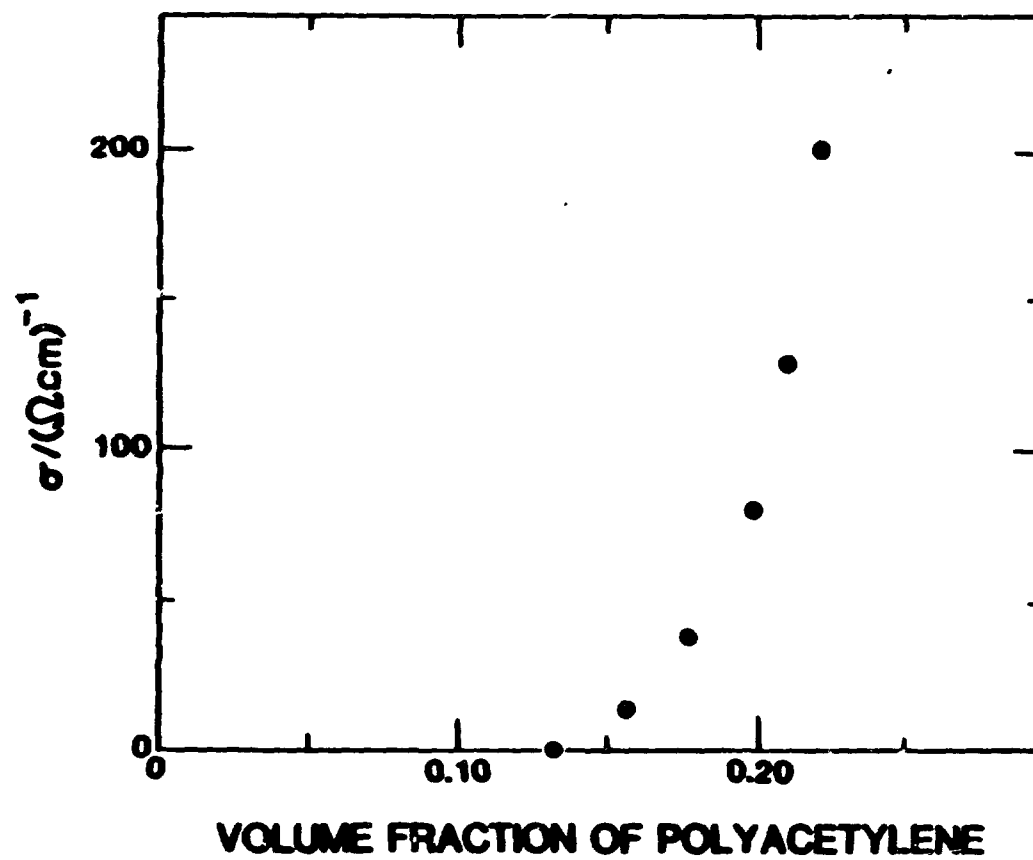| Repeat Unit		Absorption Maxima/eV			
Thierylpyrrole	p-TS/CH$_3$CN	---	1.95	---	0.7
	ClO$_4$/PC	2.65	---	1.35,1.5	0.65,0.86
Furylpyrrole	Film	2.6	2.1	1.4	0.9
	Solution	2.67	1.85	---	0.65
Thienyl 3-methylpyrrole		3.0	2.1,1.8	---	0.87,0.65

Acknowledgments

REFERENCES

1.   M. Aldissi, Synth. Metals 13, 87 (1985).
2.   M. Aldissi and A. R. Bishop, Polymer 26, 622 (1985).
3.   F. B. Schügerl and H. Kuzmany, J. Chem. Phys. 74, 953 (1981).
4.   D. B. Fitchen, Mol. Cryst. Liq. Cryst. 83, 95 (1982).
5.   L. Lauchlan, S. P. Chen, S. Etemad, M. Kletter, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. B 27, 2301 (1983).
6.   B. S. Hudson, and B. Kohler, Chem. Phys. Lett. 14, 29 (1972).
7.   P. Hofflin, T. Semb, S. J. Henderson and J. W. White, to be published.
8.   M. Aldissi and A. M. Nyitray, to appear in ACS Books Series "Electronic and Photonic Applications of Polymers".

FIGURE CAPTIONS

Fig. 1:   Conductivity as a function of polyacetylene volume fraction in doped polyacetylene-polystyrene diblock copolymers.
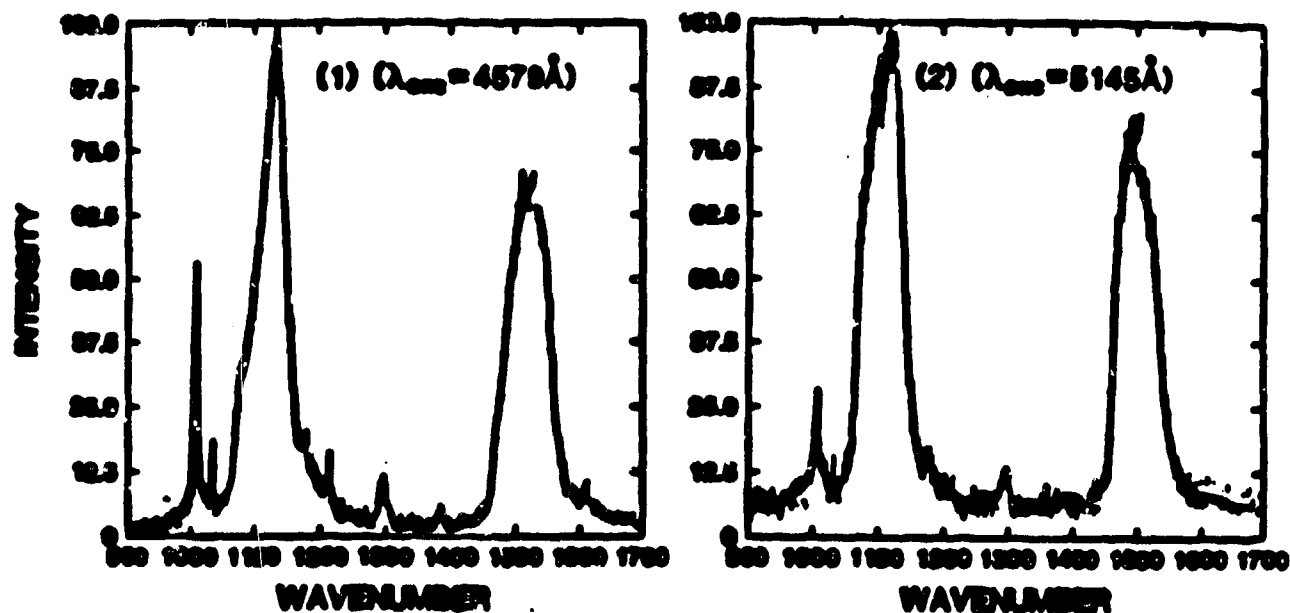
Fig. 2:   Resonance raman spectra of a polyacetylene-polyisoprene copolymer solution in toluene.

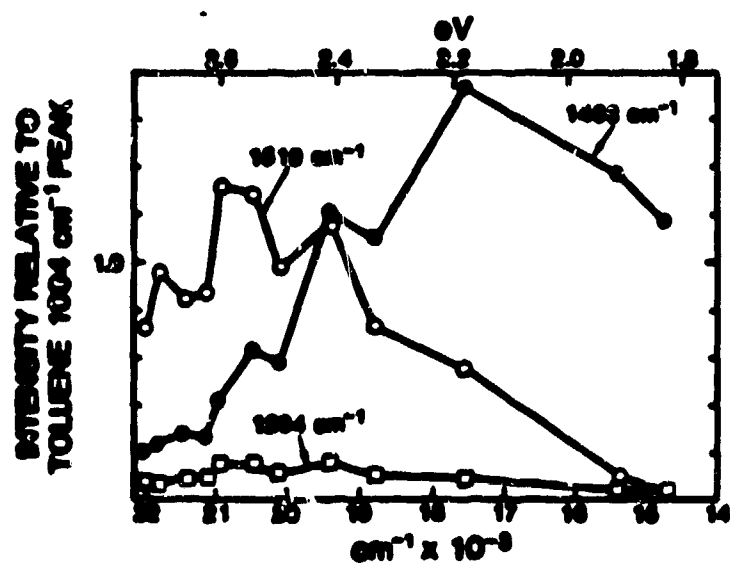Fig. 3:   Excitation profiles of the polyene characteristic peaks of a polyacetylene-polyisoprene copolymer solution in toluene.

Fig. 4:   UV-Vis. spectra of polythiophene, polypyrrole and
           poly(thienylpyrrole).

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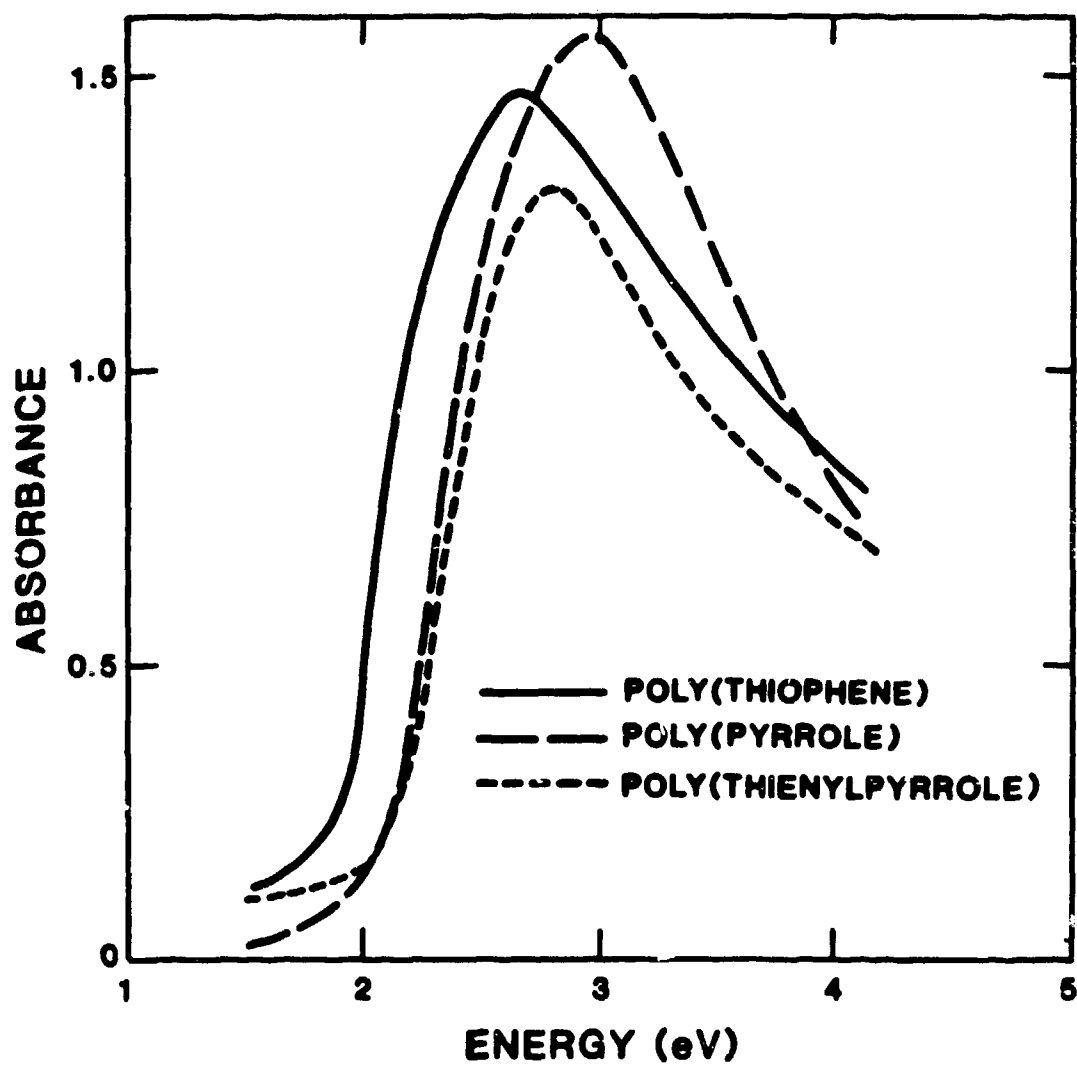

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